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Short communication

# A novel bifunctional additive for safer lithium ion batteries

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## HIGHLIGHTS

- A phosphate ester with aromatic group as a bifunctional additive is synthesized.
- RDP addition could lower the self-extinguishing time (SET) of the electrolyte.
- RDP could be electro-polymerized and postpone the voltage runaway.

## ARTICLE INFO

## ABSTRACT

A novel flame retardant, Resorcinol bis(diphenyl phosphate) (RDP), is successfully synthesized and investigated as electrolyte additive for lithium ion batteries. It is found that RDP can be electro-polymerized at 4.4 V (vs. Li/Li$^+$), which will protect the batteries from voltage runaway by consuming the overcharge current. Moreover, RDP addition could lower the self-extinguishing time (SET) of the electrolyte. The influence of proper RDP addition on the cycling performance and capacity is negligible. Thus, RDP could be used as a novel electrolyte additive for lithium ion batteries functioned as both overcharge protection and flame retardant. The results may also be helpful for the further design of advanced lithium ion battery electrolytes.

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## 1. Introduction

Lithium ion batteries are now widely used in various portable electronics and also considered as promising candidates for energy storage and electric vehicles. However, one key hindrance for further applications of Lithium ion batteries is its safety concern. Since the state-of-the-art electrolytes of lithium ion batteries use highly flammable and voltage sensitive carbonate based electrolytes, which might causes serious hazards of firing and explosion under abused conditions such as overcharge, heat, crash etc [1–3].

To solve these problems, much effort has been focused on developing safety additives such as flammable retardants [4–9] and overcharge inhibitors [10–18]. Among them, phosphates esters have been proved to be effective as flame-retardant additives for lithium ion batteries [4–7]. In the other way, many benzene derivatives were verified as applicable safety additives, which act

by forming conducting [10,11,13] or isolating polymers [15] inside the batteries to bypass or interrupt the internal current flow. If one additive can have the functions of both flame-retardant and overcharge protection, it would provide more reliable protection for Li-ion batteries in more burdensome conditions [16–19].

Based on the previous researches, by combining phosphate group and a benzene derivative, Resorcinol bis(diphenyl phosphate) (RDP) was synthesized and test as a safety additive for Li-ion batteries. It is found that this electrolyte additive can not only reduce the flammability of the electrolyte but also provide overcharge protection for 4 V class batteries. The overcharge protection mechanism is also discussed.

## 2. Experimental

RDP was synthesized by a one pot phosphorylation reaction (shown in Fig. 1), similarly to the etherification of phosphates reported in Ref. [17]. All the chemicals were of analytical grade and used without further purification except otherwise noted. In a typical experimental procedure, 0.1 mol of resorcinol, 0.24 mol of

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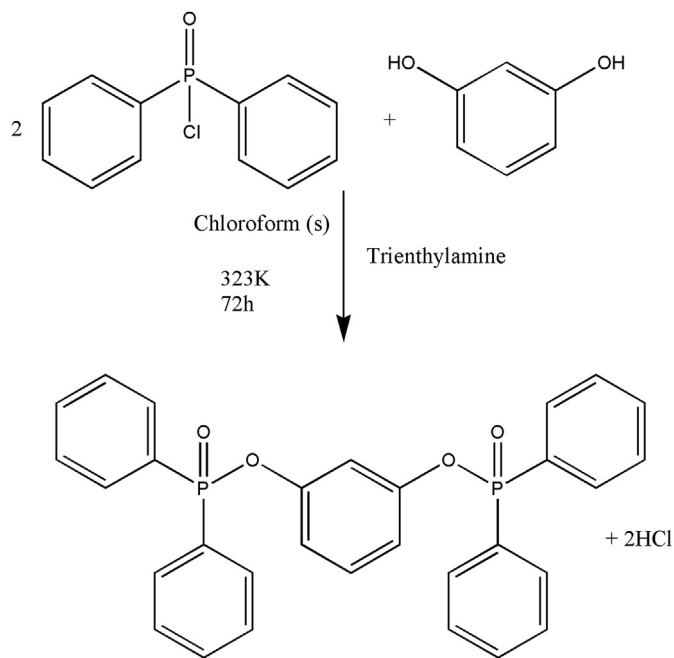E-mail address: jinkuifeng@gmail.com (J. Feng).

**Fig. 1.** Synthetic route of RDP.

triethylamine (Et$_3$N) in 100 ml of dehydrated chloroform in a three-necked 500 ml flask, and then add 0.2 mol of diphenyl chlorophosphate in the flask. The reaction mixture was stirred at 323 K for 72 h; the resultant was filtered off and then dried to give a colorless liquid, and then the product was washed with 5% HCl solution and 5% NaOH solution successively, finally purified by distillation under vacuum over molecular sieve 4 A. Yield: 85% based on resorcinol.

The FT-IR spectra of RDP were recorded on a NICOLET AVATAR360 FT-IR spectrometer with KBr pellets. Elemental analysis of RDP was performed on VarioEL III instrument. $^1$H NMR spectra of RDP were recorded on a Mercury VX-300 (300 Hz) apparatus with tetramethylsilane (TMS) as internal standard and CDCl$_3$ as solvent.

To examine the non-flammability of the RDP electrolyte, we measured the self-extinguishing time (SET) for pre-weighed samples of the electrolyte solutions, in a similar method as described in Ref. [17]. The typical procedure for SET measurements is to use the fiberglass balls (∼10 mm in diameter) to absorb 0.5 g electrolyte and then burn the fiberglass to record the burning time. Each test was repeated four times and the burning times were averaged. To study the change in morphology of the electrodes after overcharge, the electrode films were detached in the glove box, washed with tetrahydrofuran followed by drying in a vacuum at room temperature and then examined by field emission scanning electron microscopy (FE-SEM, SU-70, Hitachi, Japan).

The electrochemical window of RDP was examined by cyclic voltammetry (CV) using a stainless steel electrode as working electrode and lithium sheet as both counter electrode and reference electrode. The data acquisition and analysis were collected on a Princeton electrochemical workstation (PAR stat 2273, Ametek, USA). The conductivity of the electrolyte with and without RDP was measured and calibrated with reference to the conductivity of 0.1 M KCl solution, using a conductivity measuring meter (DDS-11A, Leici Co. Ltd, Shanghai, China).

The electrochemical compatibility of the RDP-containing electrolytes was examined by laboratory LiMn$_2$O$_4$–graphite coin type cells. The positive LiMn$_2$O$_4$ electrode was consisted of 85% LiMn$_2$O$_4$,

7% acetylene black and 8% PVDF (wt.%) and the negative graphite electrode is consist 90% graphite, 2% carbon black and 8% PVDF. The base electrolyte was 1 M LiPF$_6$/EC-EMC (1:3 v/v) purchased from Guotaihuarong Chemical, Co. Ltd. China. The charge–discharge measurements were carried out using a computer-controlled programmable battery charger (BTS-0518001 type, Shenzhen, China). To test the AC impedance of the cell at different charge states, the cell was charged to a given potential at 0.5 mA and rest for 1 h to reach a stable open-circuit voltage, and then the impedance was measured by applying a 5 mV of ac oscillation over the frequency range from 1000 kHz to 0.01 Hz.

## 3. Results and discussion

### 3.1. Physical properties and characterization of RDP

The molecular structures of RDP were confirmed by FT-IR bands (3070, 1580, 1495, 1297, 1162, 1120, 1034, 958 cm$^{-1}$), $^1$H NMR (CDCl$_3$, 300M) $\delta$: 6.1–6.8 (4H, s), 6.7–7.2 (20H, s), and MS (M$^+$, 574).

Fig. 2 shows the combustibility of the 1 M LiPF$_6$/EC-EMC electrolyte at various content of RDP. It can be seen that with increasing RDP content from 0 to 72 v%, the burning time of the electrolyte decreases from 49 to 0 s g$^{-1}$, suggesting the RDP can lower the flammability of the electrolyte significantly [2]. Phosphate compounds are known as flame retardants that can function by the combination of radical adsorption and oxygen isolation mechanism [4]. The ionic conductivity of the electrolyte decreased slightly with the increase of the RDP content, which may due to the higher viscosity of RDP and the dilute of the LiPF$_6$ concentration. To get a compromise between the ionic conductivity and non-flammability of the electrolyte, we selected 10% RDP content as a balanced content to value its electrochemical characters. Further research may be on the optimization of the side effects.

### 3.2. Electrochemical behaviors of RDP

Fig. 3 shows the electrochemical performance of LiMn$_2$O$_4$/graphite cells with the electrolytes containing different concentrations of RDP. With the increase of RDP content, the capacity and coulombic efficiency only slightly decreases due probably to the dilute of LiPF$_6$ concentrations and trace impurities.

Moreover, the electrolytes with 10% or less RDP have resulted in negligible capacity loss on cycling. Therefore, the adequate addition of 10% RDP does not bring noticeable harmful effect on the
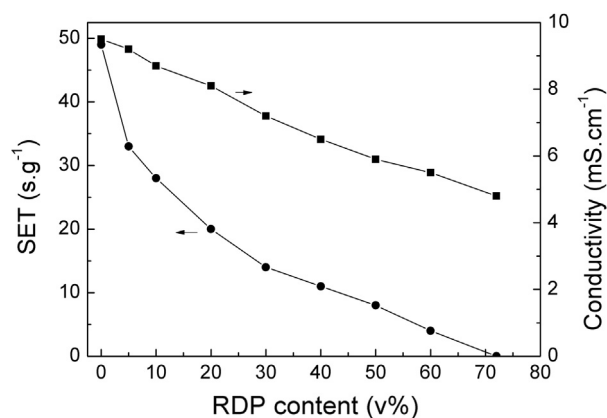


**Fig. 2.** Flammability and ionic conductivity of 1 M LiPF$_6$ EC + EMC (1:3 v/v) at different contents of RDP.
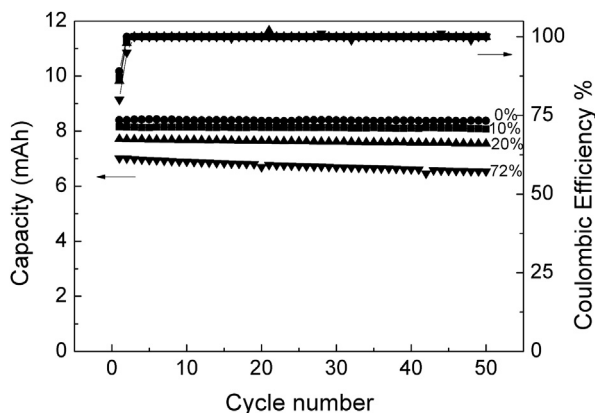
**Fig. 3.** The cycling performance, coulombic efficiency and discharge capacity of the LiMn$_2$O$_4$/graphite cells with different addition of RDP.

electrochemical performance of the cell except for lowering conductivity [4,20].

To examine the potential window of RDP, CV was performed. Fig. 4 showed the CV curves of 1 M LiPF$_6$/EC-EMC electrolyte with addition of 10% RDP. In the presence of RDP, a sharp oxidation current arose at 4.4 V (vs. Li/Li$^+$), obviously due to the electrochemical oxidation of RDP molecules. Since the oxidation potential (4.4 V) of RDP is higher than the complete charging potential of most 4 V Li-ion batteries and lower than the decomposition potentials of organic electrolytes currently used (about 5 V). Besides the redox current due to lithium deposition (−0.5 to 0 V) and dissolution (0–0.5 V) in the potential range of −0.5 and 0.5 V, there were no apparent side reactions of the RDP observed between −0.5 to 4.4 V, suggesting that RDP is quite stable in this potential range. We can use RDP as an overcharge protection additive for overcharge protection of most 4 V class Li-ion batteries. Once the Li-ion batteries are overcharged to 4.4 V, the RDP molecules begin to be electro-polymerized on the cathode electrode (as shown in the inner graph of Fig. 4), which will consume the overcharge current in the batteries and the resulting polymer product is mostly electronically conductive, as it was reported in the case of electrochemical polymerization of other dialkoxybenzene compounds [11].
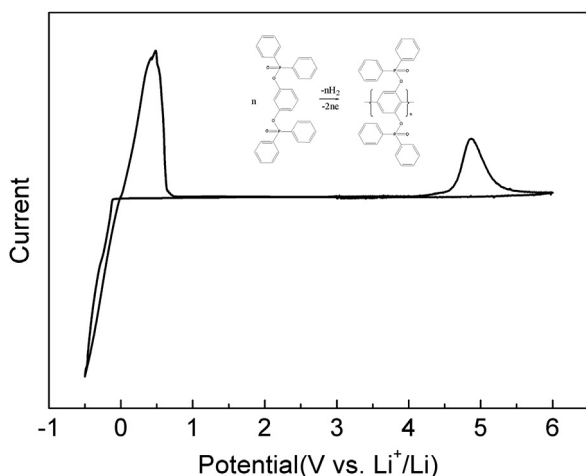
Fig. 5 compares the LiMn$_2$O$_4$–graphite cells using the blank and the 10% RDP added electrolyte. Both types of the cells were first cycled between 3 and 4.3 V (vs. Li$^+$/Li) at 50 mAh g$^{-1}$ before overcharged to 5 V. The charge/discharge capacity of the cells is (9.2 mAh/8.1 mAh) and (9.5 mAh/7.8 mAh), respectively, with a similar curve. It can be seen that there is no much difference between these cells during normal charge and discharge, indicating that the 10% RDP addition has no much affection on the normal cell performance. However, when overcharged, the voltage of the cells using blank electrolyte rises up sharply to 5 V, at which the decomposition of electrolyte starts [11]. Since the electrolyte decomposition is exothermic and can produce a large number of flammable gases, the prolonged overcharge is no doubt a direct cause for hazardous behaviors of the cells [3,4]. In contrast, for the cells using 10% RDP added electrolyte, the charge voltage starts to stabilize from about 4.4 V and does not goes up to 5 V even after 100% overcharge, suggesting effective overcharge protection ability. Since the protection voltage is accordance with the electrochemical oxidation voltage of RDP, it is reasonable to attribute the protection ability to the electrochemical polymerization of RDP.

The surface morphology of the pristine and overcharged cathode was investigated by SEM. As shown in Fig. 6, for the pristine cathode, the electrode exhibits a porous structure with well dispersed LiMn$_2$O$_4$ among carbon black conductive agent (Fig. 6(a)). However, after overcharged to 4.6 V in electrolyte with 10% RDP, the electrode surface was fully covered with thick polymer (Fig. 6(b)), which obvious results from the electro-oxidation of RDP. As an aromatic molecule, the electrochemical oxidation of RDP molecules commonly results in electro-polymerization mechanism, as it was reported in the case of electrochemical polymerization of dialkoxybenzene compounds [11,12,15,17]. The polymerization will consume the overcharge current and delay the cell from overcharge abusement.

However, at the late stage of overcharge, the voltage of the cell with RDP finally went up, to further examine the actual overcharge protection behavior of RDP, electrochemical impedance spectroscopy (EIS) is performed, in which a small sinusoidal voltage stimulus is applied to an electrochemical cell and its response in terms of current is measured. In the EIS study, impedance data of the cells with or without 10% RDP added electrolyte was measured after being charged to 4.3 V and 4.6 V, and the results are given in Fig. 7. A typical impedance spectrum of LiMn$_2$O$_4$/graphite cell shows two over-lapped semicircles through high to middle frequency followed
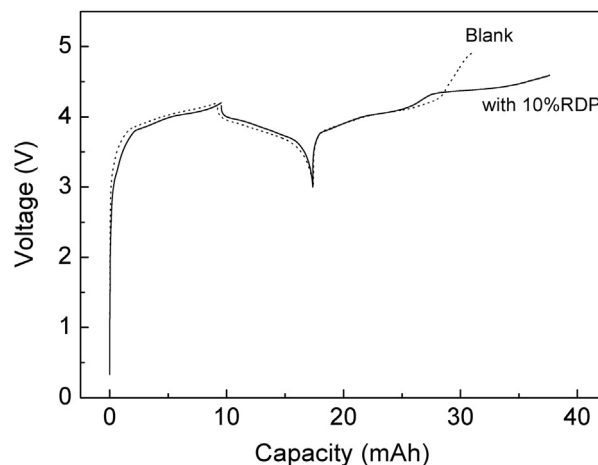


**Fig. 4.** CV curves of 1 M LiPF$_6$ EC + EMC with 10% RDP and the electro-polymerize mechanism of RDP (inner graph).



**Fig. 5.** Normal charge/discharge and overcharge of LiMn$_2$O$_4$/graphite coin cells. The electrolyte was 1 M LiPF$_6$ EC + EMC (1:3 v/v) containing (dash line) no additive (solid line) 10 v% RDP, respectively.
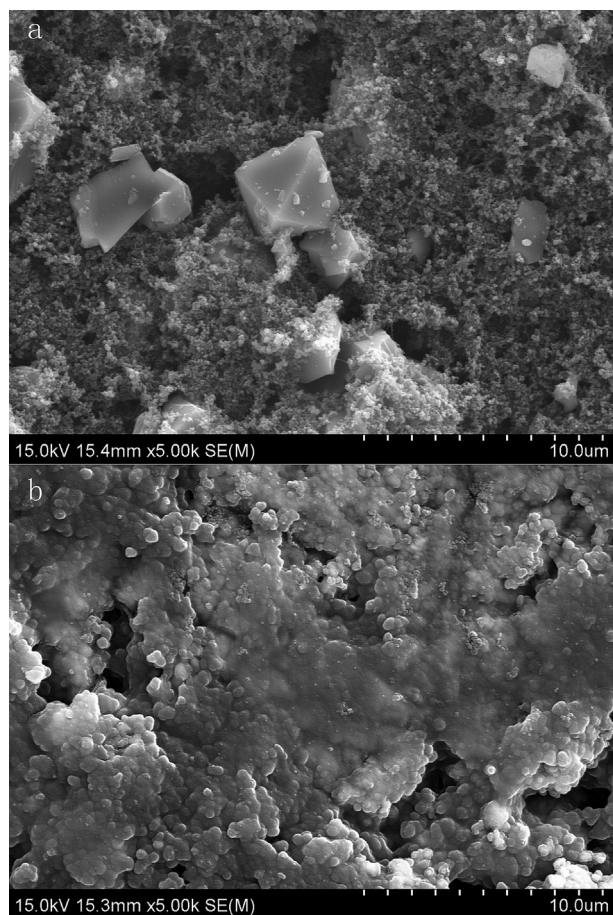
**Fig. 6.** SEM images of the LiMn$_2$O$_4$ electrode taken from the overcharged cells with (a) no additives, and (b) 10% RDP electrolyte.

by a straight sloping line at low frequency. The semicircle at high frequency, could be attributed to resistance ($R_{SEI}$) and capacitance ($C_{SEI}$) of the solid electrolyte interface (SEI) formed on the surface of two electrodes. The semicircle at medium frequency could be attributed to charge-transfer resistance ($R_{ct}$). Warburg impedance, which corresponds to the straight sloping line at low frequency, could be related to diffusion of lithium ions in the active material particles [21,22]. From the figure we can see that for the cell with
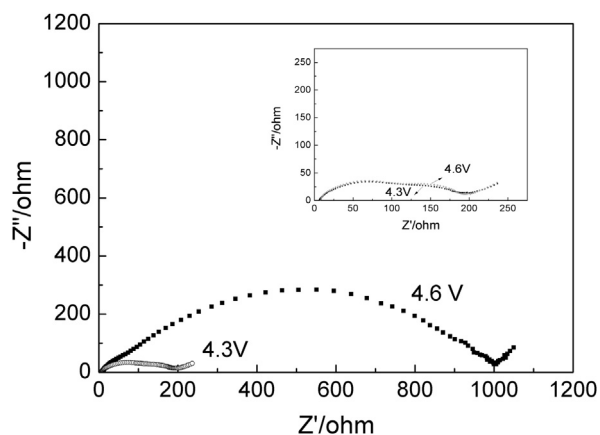
10% RDP added electrolyte, when charged to 4.3 V, the LiMn$_2$O$_4$/graphite showed interfacial impedance ($C_{SEI}$ $R_{SEI}$) of about 135 Ω and charge-transfer impedance ($R_{ct}$) of about 90 Ω. When the cell is charged to 4.6 V, the interfacial impedance ($C_{SEI}$ $R_{SEI}$) slightly increases to about 145 Ω, however, the charge transfer resistance ($R_{ct}$) dramatically rise up to about 950 Ω, which is ten times higher than the value at 4.3 V. For comparison, the impedance of the cell using blank electrolyte remains almost unchanged from 4.3 V to 4.6 V (inner graph), as the cell is in a fully charged conditions. The sharp increase in the charge transfer resistance ($R_{ct}$) can be ascribed to the fact that the polymer formed on the cathode by RDP is nonconductive, thus inhibits the charge transfer process. As a consequence, the cell voltage gradually rises up [11,15]. In another way, as the highly oxidative cathode and electrolyte is separated by inert polymer, thermal runaway due to contact reaction may be alleviated [13].

## 4. Conclusions

A bifunctional additive, RDP, is synthesized and characterized as a safety additive for lithium-ion batteries. Results demonstrated that RDP addition could significantly lower the flammability of the electrolyte and therefore enhance the thermal stability of the Lithium ion batteries. Besides, RDP can also be electro-polymerized at 4.4 V (vs. Li/Li$^+$) and consume the overcharge current, which will protect the batteries from voltage runaway. Therefore, RDP could be used as a novel safety additive for advanced lithium-ion batteries.

## Acknowledgment

**Fig. 7.** Changes in Nyquist plots of LiMn$_2$O$_4$/graphite cells with and without (inner graph) RDP at 4.3 V and 4.6 V.

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